Modeling of Ammonia Emissions from Soils

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ABSTRACT

Using a dynamic flow-through chamber system in conjunction with a Thermo Environmental 17C Chemi-luminescence ammonia (NH_3) analyzer, emissions from slurry-amended, that is, effluent from the lagoon ($\sim$33 kg N ha^{-1}) and nonamended soils were calculated at a swine farm in eastern North Carolina. The average NH_3-N flux values during the period when the soils were not amended with any slurry were $\sim$54 ng N m^{-2} s^{-1}, while the average NH_3-N flux values measured immediately following the application of slurry to the soil were 1723.9 ng N m^{-2} s^{-1}. An empirical model relating soil temperature to NH_3 flux for nonamended soils explained over 70% of the variability in NH_3 emissions; however, a similar empirical model relating soil temperature to NH_3 flux for slurry-amended soils was able to explain only 39% of the variability in NH_3 emissions. A mass transport model, based on physical and chemical processes to estimate NH_3 emissions from recently amended soils is also presented and compared and contrasted to the empirical model. The variables used in the mechanistic model are pH, soil temperature, and total ammoniacal nitrogen content. When using the mass transport model, the percentage difference between predicted and measured values for the nonamended and slurry-amended soils were 164 and 16%, respectively, indicating that the mechanistic model is only applicable for periods when nitrification/denitrification, plant uptake, and immobilization are small enough in comparison to the chemical and physical processes following slurry application that they can be ignored. The percentage of the nitrogen (N) applied, which was emitted as NH_3, increased at its greatest rate immediately following slurry application (1–2 days) and then began to level out at a value of approximately 20% by day 4. Previous laboratory studies found these volatilization events to be short lived (few days–2 weeks), and this study corroborates those findings.

Key words: ammonia; biogenic emissions; agricultural emissions; modeling; nitrogen; dynamic flow-through chamber

INTRODUCTION

Emissions of ammonia (NH_3) from soils have been found to be a significant source of NH_3 into the atmosphere (Table 1). The vast majority (approx. 90%) of the NH_3 in the atmosphere is converted into NH_4^+ aerosols by the irreversible reactions of ammonia with sulfuric acid (H_2SO_4), nitric acid (HNO_3), hydrochloric acid
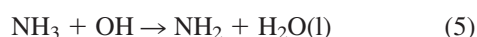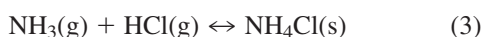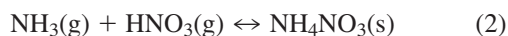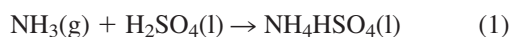
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Table 1. Global tropospheric NH$_3$ budget.

Source	NH$_3$[b]	Sink	NH$_3$[b]
Coal combustion	2	Wet deposition	46
Automobiles	0.2	Dry deposition	10
Biomass burning	5	Reaction with OH	1
Domestic animals	32		
Wild animals	—		
Human excrements	4		
Soil/plant emissions	10		
Fertilizer losses	9		
Oceans	13		
Total sources[a]	75	Total sinks	57

[a]It is accepted that the apparent difference between total NH$_3$ sources and sinks represents uncertainties in identified budget terms, not atmospheric accumulation; [—] Indicates insignificant or unavailable terms; (1 Tg = 10^{12} g); source: [b]Schlesinger and Hartley, 1992; source modified from Warneck, 2000.

(HCl), water, and to a lesser extent (approximately 10%), the hydroxyl radical (OH) in the atmosphere (Warneck, 2000). These NH$_4^+$ aerosol producing reactions can be summarized as follows:

$$NH_3(g) + H_2SO_4(l) \rightarrow NH_4HSO_4(l) \quad (1)$$

$$NH_3(g) + HNO_3(g) \leftrightarrow NH_4NO_3(s) \quad (2)$$

$$NH_3(g) + HCl(g) \leftrightarrow NH_4Cl(s) \quad (3)$$

$$NH_3(g) + H_2O(l) \rightarrow NH_4^+ + OH^- \quad (4)$$

$$NH_3 + OH \rightarrow NH_2 + H_2O(l) \quad (5)$$

(Finlayson Pitts and Pitts, 1986).

The conversion of NH$_3$ to NH$_4^+$ dictates the spatial scale of the contribution of NH$_3$ to the total atmospheric nitrogen input (Aneja *et al*., 2001b). Due to ammonia's relatively shorter lifetime in the atmosphere (less than 5 days), low source height and high deposition velocities, its distribution is usually limited to its nearby surroundings (Warneck, 2000; Aneja *et al*., 2001b). The NH$_4^+$ aerosols, however, have lifetimes on the order of 15 days, and therefore can travel and deposit at larger distances from the ammonia source.

Although nitrogen is a critical nutrient for the survival of micro-organisms, plants, animals, and humans, it can cause detrimental effects when concentrations reach excessive levels (Pearl, 1997; Erisman *et al*., 1998). Some of the consequences associated with elevated concentrations and depositions of reduced N species are:

1. Respiratory disease caused by exposures to high concentrations of photochemical oxidants and fine particulate aerosol (e.g., PM 2.5)
2. Nitrate contamination of drinking water
3. Eutrophication, harmful algal blooms, and decreased surface water quality
4. Nitrogen saturation of forest soils

(Erisman *et al*., 1998). In addition to the damaging environmental consequences, the loss of NH$_3$ represents an economic loss to the farmer, as the emitted nitrogen is no longer available to the plant.

North Carolina has recently experienced a large increase in total number of swine and is currently the United States' second largest swine producing state (Fig. 1). NH$_3$ emissions from these confined animal feeding operations (CAFOs) have been estimated to represent approximately 46% of the NH$_3$ budget in North Carolina compared to the national average of 10% [Fig. 2(a) and (b)]. Current methods employed to develop these budgets involve the use of European-based emission factors applied to animal populations. Although attempts have been made to try and apportion the NH$_3$ between the various emission pathways of a swine operation (Fig. 3), the emission factors currently used still contain a high degree of uncertainty.

Control strategies to minimize NH$_3$ emissions require a more thorough understanding of the relative source strengths of the various emission pathways. Furthermore, computers used to model the fate of this increased ammonia can only be as accurate as the input data, and failing to capture any of the spatial or temporal variability in the NH$_3$ emissions will result in poor model output. This study describes a mass transport model, relating NH$_3$ release from the soil to the soil nitrogen content, pH, and soil temperature. The model will then be assessed with field measurements with the aim of gaining a better understanding of the physical and chemical processes controlling the NH$_3$
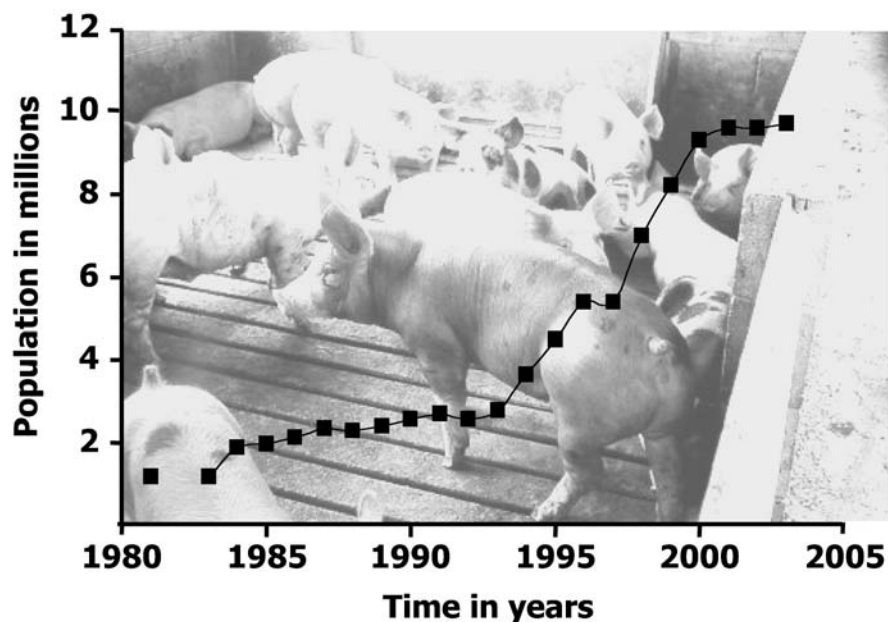
Figure 1. Swine population in North Carolina. (Source: North Carolina Agricultural Statistics, NCDA, 2001.)

emissions from soils and the applicability of this proposed mass transfer model.

EXPERIMENTAL PROTOCOLS

Sampling site and sampling scheme

The NH_3 flux measurements were made at the Upper Coastal Plain Research Station, located in Edgecombe County, North Carolina (see Fig. 4 for measurement location; see Table 2 for site/soil characteristics). This facility (contains approximately 178 hectares, 101 of which are cropland soils) is operated with typical agronomic and husbandry practices for the respective crops and animals. The facility also maintains a farrow-to-finish swine operation, with approximately 1,250 swine on site. The waste from the animals (urine and feces) is flushed from the swine production houses into two uncovered anaerobic waste treatment and storage lagoons (a primary and secondary lagoon, total acreage ~1 hectare). The effluent from these lagoons is periodically sprayed to the crops as a nutrient source. A corn crop was harvested on August 21st, and the stalks were shredded and left on the soil surface. No cover crop was planted, nor was the field fertilized throughout the winter and Spring of 2001.

NH_3 concentration measurements were made on 13 randomly selected plots located within a 10-m radius of a mobile laboratory (Modified Ford Aerostar Van, temperature controlled to within the operating range of the instru-

ments). Portions of the research facility were being sprayed with the slurry during this measurement period. For the purposes of this study and to avoid contamination of the research equipment, the plots used in this study were amended individually. Twelve of the plots were surface applied (uniform spreading on surface) with 750 mL of slurry collected from the hog waste lagoon and the last plot, which was used as the control, was unamended. Based on chemical analysis conducted on April 25, 2001, by the North Carolina Agronomy Division, this equated to approximately 33 kg N ha^{-1}, an amount representative of typical agronomic practices (Troeh and Thompson, 1993).

A daily experiment consisted of placing the chamber on the stainless steel collar, which had been inserted into the soil the previous evening. The dynamic chamber used in this study is a fluorinated ethylene propylene (FEP) Teflon-lined (5-mil thick) open bottom cylinder (diameter ~27 cm, height ~42 cm, and volume ~25 L). The chamber penetrated the soil surface to a depth of ~4 cm forming a seal between the soil surface and the air within the chamber. The placement of the chamber on the soil surface was performed in a statistically random manner (Aneja *et al.*, 2000). The collars were all located on bare soil, with no plants being enclosed within the collar or chamber system. The chamber was placed on the collar at approximately 8:00 a.m. and flushed with zero grade air (i.e., contains no ammonia) for at least 1 h before data collection began at 9:00 a.m. This sampling scheme ensured that the concentrations within the chamber reached

steady state prior to any data acquisition and allowed for the instruments to undergo their daily calibrations. Daily experiments ended at approximately 5:00 p.m., and the stainless steel collar was relocated to a random location within a 10-m radius of the mobile laboratory, in preparation for the next day's experiment. This procedure allowed a minimum of 16 h for any effect on soil NH_3 flux,

due to soil disturbances caused by the insertion of the stainless steel collar, to dissipate.

Instrumentation and flux calculation

The chamber design, associated mass balance equation, and calibration procedures are described in full in Roelle *et al.* (1999).
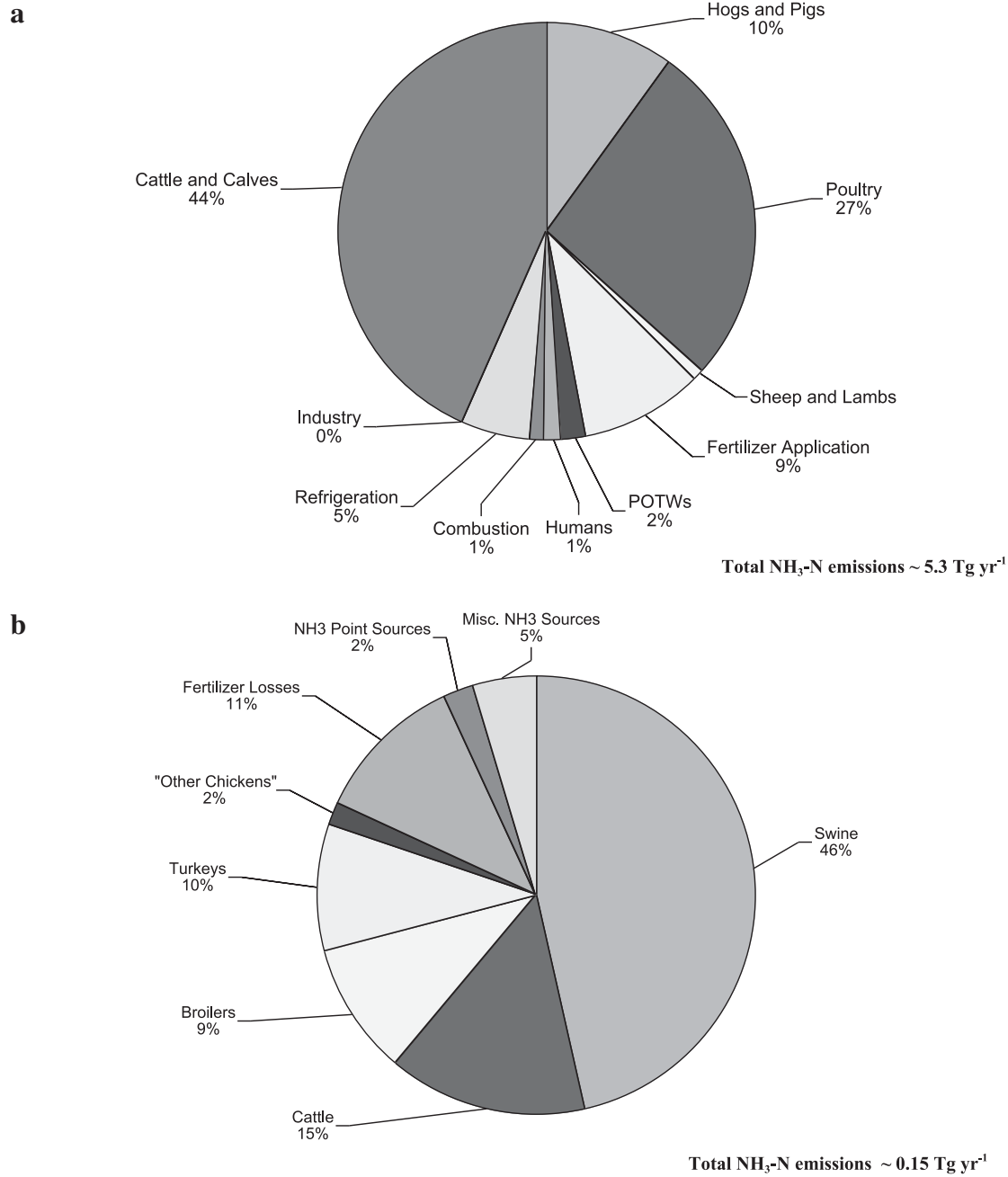

a

Hogs and Pigs
10%

Cattle and Calves
44%

Poultry
27%

Industry
0%

Sheep and Lambs

Fertilizer Application
9%

Refrigeration
5%

Combustion
1%

Humans
1%

POTWs
2%

Total NH_3-N emissions ~ 5.3 Tg yr^{-1}

b

NH3 Point Sources
2%

Misc. NH3 Sources
5%

Fertilizer Losses
11%

"Other Chickens"
2%

Turkeys
10%

Swine
46%

Broilers
9%

Cattle
15%

Total NH_3-N emissions ~ 0.15 Tg yr^{-1}

Figure 2.   (**a**) Percent of Ammonia-Nitrogen from various sources in the United States for 1994. (Source: Battye *et al.*, 1994.) (**b**) Percent of Ammonia-Nitrogen from various sources in North Carolina for 1996. (Source: Aneja *et al.*, 1998.)
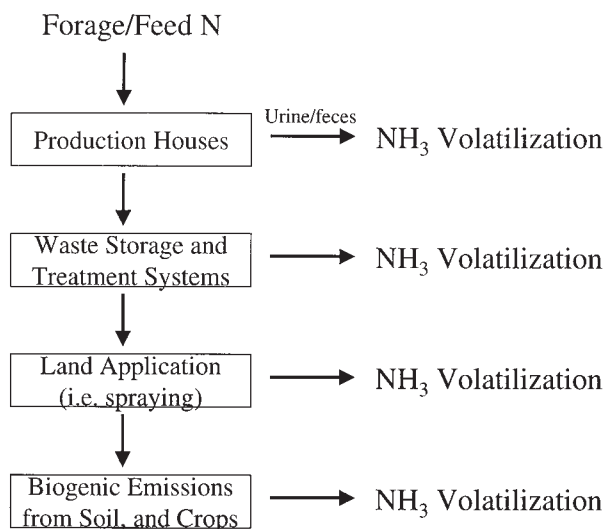
Forage/Feed N

Production Houses → Urine/feces → NH_3 Volatilization

Waste Storage and Treatment Systems → NH_3 Volatilization

Land Application (i.e. spraying) → NH_3 Volatilization

Biogenic Emissions from Soil, and Crops → NH_3 Volatilization

Figure 3. Major routes for NH_3 emissions from intensively managed animal operations in North Carolina, USA. (Source: Aneja *et al.*, 2001a.)

Soil analysis

A soil sample (top 2 cm) was taken from the center of the chamber footprint at the end of each measurement period (approximately 1 sample per day), and analyzed for soil pH, soil moisture, NH_x ($NH_x = NH_4^+ + NH_3$), NO_3-N, and Total Kjeldahl Nitrogen (TKN = organic N + NH_3^- N + NH_4^+-N) by the North Carolina State University Department of Biological and Agricultural Engineering. Based on previous studies, the unamended plots are found to remain fairly consistent in terms of pH and N-content, and therefore, the unamended plot was only sampled once. Soil temperature was measured with a Campbell Scientific temperature probe (accuracy $\pm$ 3%) inserted into the soil to a depth of approximately 5 cm. Air temperatures (Campbell Scientific, Logan, UT; accuracy $\pm$ 3%) were measured inside of a radiation shield at a height of 1.5 meters. Data was stored in 15-min binned averages utilizing a Campbell Scientific 21X Micrologger, in conjunction with a Toshiba laptop computer.

MODEL

The exchange of NH_3 gas from the soil into the atmosphere is assumed to be related to the resistances in both the liquid and gas phases and the gas concentration gradient between the soil–air interface. The mechanistic model describing this exchange can be written as:

$$\text{Flux}(NH_3)_{gas} = K([NH_3]_{(gas,soil)} - [NH_3]_{(gas,air)}) \quad (6)$$

where K is the transfer coefficient from the NH_3 gas in the soil to the NH_3 gas in the air (Singh and Nye, 1986a). Total ammonia ($NH_x = NH_3 + NH_r^+$) in the soil is dependent on the plant uptake rate, immobilization rate, nitrification/denitrification rates, and volatilization of the gas from the soil (Sherlock and Goh, 1985). Previous researchers have shown that during the time period immediately following fertilization (4 days to 2 weeks), the volatilization process is sufficiently strong so that other processes (plant uptake, immobilization, nitrification/denitrification) can be neglected (Sherlock and Goh, 1985). Furthermore, following slurry application the $[NH_3]_{(gas,soil)}$ will generally be significantly larger than the $[NH_3]_{(gas,air)}$ and the NH_3 flux equation can be rewritten as:

$$\text{Flux}(NH_3)_{gas} = K[NH_3]_{(gas,soil)} \quad (7)$$

Therefore, the determination of the NH_3 flux from the soil is dependent on knowing the NH_3 gas concentration in the soil/slurry environment and the exchange coefficient K.

The NH_3 gas concentration in the soil solution can be calculated by examining the chemical equilibrium between NH_3 and NH_4^+. As slurry is initially applied to the soil, it is rapidly hydrolyzed to produce ammonium ions in the soil:

$$(Urea) \longrightarrow NH_4^+{}_{(aq)} \quad (8)$$
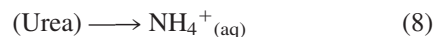
The subsequent dissociation of NH_4^+ in the solution can be described by:

$$NH_4^+ + H_2O \xrightleftharpoons{K_{NH4^+}} NH_{3(aq)} + H_3O^+{}_{(aq)} \quad (9)$$

where K_{NH4^+} is the equilibrium constant and is given by:

$$K_{NH4^+} = \frac{[NH_{3(aq)}][H_3O^+{}_{(aq)}]}{[NH_4^+{}_{(aq)}]} \quad (10)$$

The ammonium equilibrium constant is found to be dependent on temperature through the following equations described by Bates and Pinching, 1950; Hales and Drewes, 1979; Aneja *et al.*, 2001a.

$$K_{NH4^+} = 5.67 \cdot 10^{-10} \cdot \exp\left[-6286 \cdot \left(\frac{1}{273.15+T_{soil}} - \frac{1}{298.15}\right)\right] \quad (11)$$

or similarly

$$\log(K_{NH4^+}) = -0.09018 - \frac{2729.92}{T} \quad (12)$$

where T is the soil temperature in Kelvin.

This first-order equilibrium between $NH_4^+{}_{(aq)}$ and $NH_{3(aq)}$ is extremely fast, and in terms of the volatilization, it will not be rate limiting (Sherlock and Goh, 1985).

The total ammoniacal nitrogen content of the soil ($NH_{x(aq)}$) can be rewritten as:

$$NH_{4^+(aq)} = NH_{x(aq)} - NH_{3(aq)} \quad (13)$$

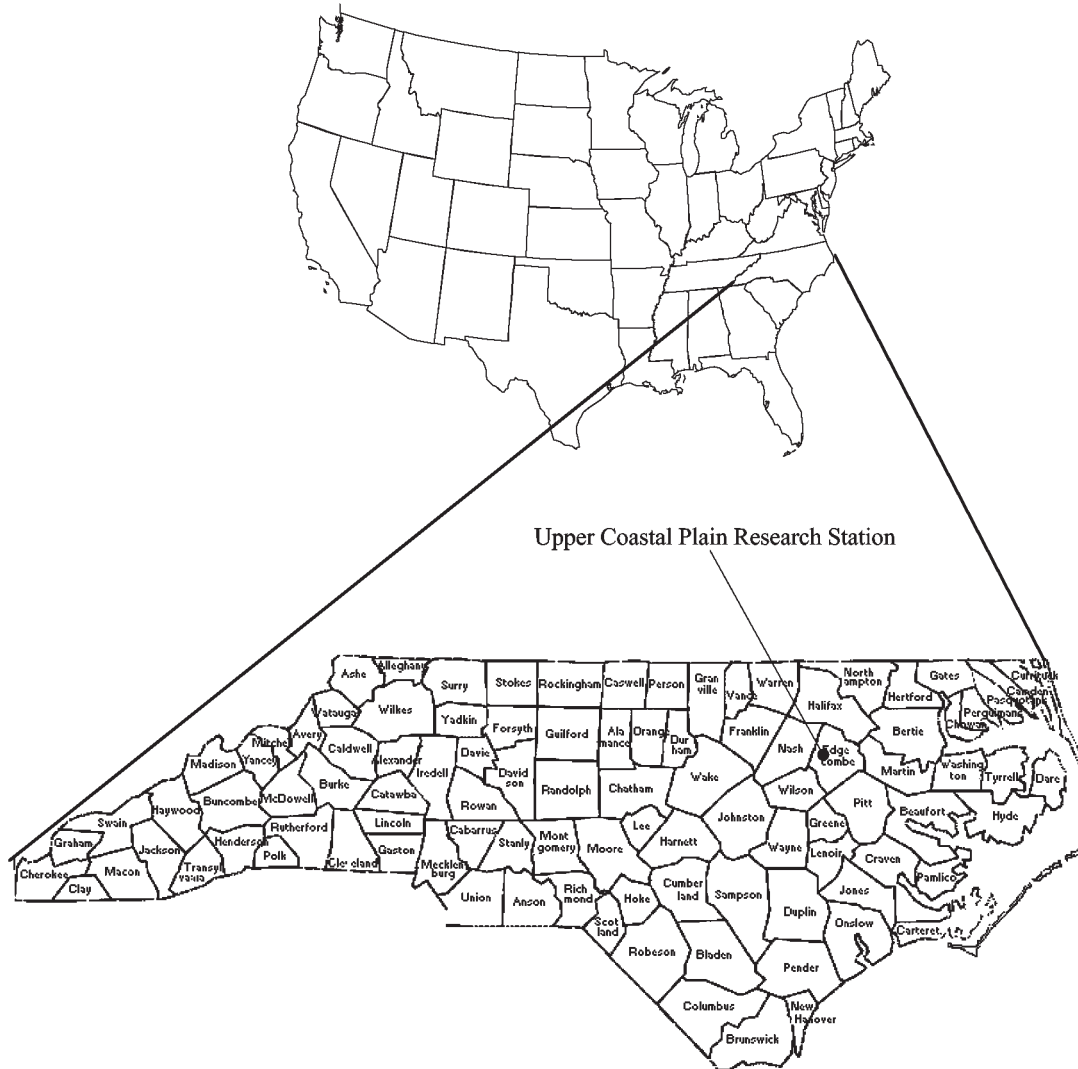**Figure 4.** Site of Upper Coastal Plain Research Station.

and substituting Equation (13) into Equation (10) yields:

$$\frac{[NH_{3(aq)}][H_3O^+_{(aq)}]}{K_{NH4^+}} = [NH_{x(aq)}] - [NH_{3(aq)}] \quad (14)$$

Solving for $NH_{3(aq)}$, Equation (14) can be rewritten as:

$$[NH_{3(aq)}] = \frac{[NH_{x(aq)}]}{\left(1 + \dfrac{H_3O^+}{K_{NH_4^+}}\right)} \quad (15)$$

Recognizing that H_3O^+ will also hydrolyze to produce H^+ ions and that $H^+ = 10^{-pH}$, Equation (15) can be rewritten in the form:

$$[NH_{3(aq)}] = \frac{[NH_{x(aq)}]}{1 + \dfrac{10^{-pH}}{K_{NH_4^+}}} \quad (16)$$

Substituting for the equilibrium constant $K_{NH_4}^+$ from Equation (12), we are left with:

$$NH_{3(aq)} = \frac{[NH_{x(aq)}]}{1 + 10^{(0.09018 + \frac{2729.92}{T} - pH)}} \quad (17)$$

At the interface of the air and liquid film in the soil solution, the aqueous NH_3 concentration is assumed to be related to the gaseous NH_3 concentration through Henry's Law equilibrium, where:

$$NH_{3(gas)} = [H] \cdot [NH_{3(aq)}] \quad (18)$$

and the Henry's Law equilibrium constant H can be expressed as:

$$Log(H^{-1}) = -1.69 + \frac{1477.7}{T}$$

(Hales and Drewes, 1979).

Table 2. Site and soil characteristics for the Spring 2001 measurement campaign at the Upper Coastal Plain Research Station, Edgecombe County, NC.

Site: Upper Coastal Plain Research Station
35.9° N. latitude
77.7° W. longitude
Elevation: 35.5 meters
Soil Type: Norfolk loamy sand

Sampling period	n	pH	% Moisture content	[NH$_x$]	N-content μg/g NO$_3$-N	TKN	Soil temp (°C)	NH$_3$ flux (ng N m^{-2} s^{-1})
30 April—Plot 1	4	6.48	13.39	105	7.81	882	23.8 ± 0.3	3390.8 ± 98.5
30 April—Plot 2	4	6.46	11.83	86	8.88	882	24.1 ± 0.02	2813.2 ± 100.0
30 April—Plot 3	4	6.77	12.19	95	8.88	906	24.6 ± 0.1	2200.4 ± 177.5
30 April—unamended	4						23.1 ± 0.2	87.3 ± 20.8
1 May—Plot 4	4	6.41	6.96	79.7	22.76	980	17.9 ± 0.7	2114.4 ± 136.4
1 May—Plot 5	4	6.54	5.32	84	15.07	828	18.2 ± 0.6	1708.7 ± 40.1
1 May—Plot 6	4	6.55	4.93	78.3	26.42	1028	18.5 ± 0.2	2323.8 ± 18.9
1 May—unamended	4						17.4 ± 0.1	71.3 ± 23.4
2 May—Plot 7	4	6.36	6.79	94.3	18.3	996	19.1 ± 0.7	1199.1 ± 12.0
2 May—Plot 8	4	6.2	7.33	73	17.07	943	19.4 ± 0.2	1071.0 ± 47.1
2 May—Plot 9	4	6.17	7.98	69.7	18.55	861	19.7 ± 0.1	1273.0 ± 124.6
2 May—unamended	4						18.6 ± 0.2	80.3 ± 19.2
3 May—Plot 10	4	6.1	4.6	59	33.2	924	17.9 ± 0.8	791.2 ± 32.3
3 May—Plot 11	4	5.95	4.08	82	29.15	976	18.1 ± 0.7	556.1 ± 9.5
3 May—Plot 12	4	6.29	4.26	76	42.27	1200	18.3 ± 0.6	1245.1 ± 4.1
3 May—unamended	4	5.4	1.19	6.03	12.93	1072	17.3 ± 0.2	67.4 ± 15.4

TKN = Total Kjeldahl nitrogen = organic N + NH$_3$-N + NH$_4^+$-N.

Substituting the Henry's Law relationship [Equation (18)] into the flux Equation (7) yields the following expression for NH$_3$ flux:

$$\text{Flux}(\text{NH}_{3(\text{gas})}) = K \cdot [\text{NH}_{3(\text{aq})}] \cdot [H] \qquad (19)$$

Substituting the NH$_{3(\text{aq})}$ from Equation (17) into Equation (18) yields the following NH$_3$ flux equation:

$$\text{Flux}(\text{NH}_{3(\text{gas})}) = \frac{K \cdot [\text{NH}_{x(\text{aq})}] \cdot [H]}{(1 + 10^{(0.09018 + \frac{2729.92}{T} - \text{pH})}} \qquad (20)$$

The mass transport model given in Equation (20) is the same model used by Aneja *et al.* (2001a) for estimating NH$_3$ flux from lagoon surfaces. While all parameters in Equation (20) can be measured or calculated in both the lagoon and soil environments, the flux is critically dependent upon accurate representation of the mass transfer coefficient (K), and the value of the Henry's law coefficient (H). Aneja *et al.* (2001a) used the two-film theory, which accounts for the role of air velocity and

temperature in the gas (k_g) and liquid phase (k_L) resistance to NH$_3$ transfer across an interface and is given by the following equation:

$$K = \left(\frac{H}{k_I} + \frac{1}{k_g} \right)^{-1} \qquad (21)$$

In a review of over 30 publications, it was discovered that the reported values of this overall mass transfer coefficient ranges from 1.3×10^{-6} m s^{-1} to 1.2×10^{-2} m s^{-1}. Several researchers have attempted to relate this overall mass transfer coefficient to various properties such as roughness length, friction wind velocity, and height of the internal boundary layer (van der Molen *et al.*, 1990; Olesen and Sommer, 1993). Using a micrometeorological technique, Svensson and Ferm (1993) calculated mass transfer coefficients from soils amended with manure and reported values ranging from 4.3×10^{-3} m s^{-1} to 1.2×10^{-2} m s^{-1}. Researchers in a laboratory using swine manure, however, reported the overall mass transfer coefficient to range between 1.3×10^{-6} m s^{-1} and 5.2×10^{-6} m s^{-1} (Zhang,

1992). Great variability does exist in the range of reported values. However, conditions during which these measurements were made do differ. In general, a review of these published reports indicated that for the slurry mixture alone, values of the overall mass transfer coefficient were on the order of 10^{-6} m s^{-1}–10^{-5} m s^{-1}, while field and laboratory experiments on slurry/soil mixtures were on the order of 10^{-4} m s^{-1}–10^{-3} m s^{-1}.

Singh and Nye (1986b) described a controlled laboratory experiment in which the exchange coefficient was measured under a variety of flow and pH conditions. These researchers reported that the value of K increased linearly as the flow rate over the soil surface increased from 0 to 1 L min^{-1}. However, they reported that as flow rates increased beyond 1 L min^{-1}, the rate of increase becomes smaller, and begins to level out at a value of 3.7×10^{-3} m s^{-1}. Sherlock and Goh (1985) theorized that in soils, water movement and the diffusion of ions is probably more restricted than in flooded soils or water bodies. Therefore, they concluded that volatilization of NH_3 from nonflooded soils is more likely to be controlled by the rate of diffusion through the soil than on wind speed.

Numerous studies conducted by Denmead *et al.* (1974) and Beauchamp *et al.* (1978, 1982) reported no positive relationships between wind speed and NH_3 emissions from nonflooded soils. Given the good reproducibility of the measurements in the experiments conducted by Singh and Nye (1986b) ($\pm 6\%$), their experimentally measured value of 3.7×10^{-3} m s^{-1} will be used in this study. For comparison purposes, the NH_3 flux using the empirically determined K value based on temperature and wind speed [Equation (21)] and as described by Aneja *et al.* (2001a) will also be presented.

RESULTS AND DISCUSSION

Temperature

Positive relationships between the release of nitrogen trace gases from soils and soil temperature are well established in the literature. For example, the solid line (plotted on a logarithmic scale) in Fig. 5 shows this temperature dependence in an empirical model [$\text{Log}_{10}(NH_3 - N \text{ Flux}) = 0.054 \cdot T_{\text{soil}} + 0.66$; $R^2 = 0.71$] developed by Roelle and Aneja (2002). This empirical model was developed from measurements made at the same measurement location as this slurry-amended study and was conducted during two different seasons (Winter and Spring, 2000) when no fertilizer (slurry or chemically derived) was applied to the soil (within 3 months of data collection). The R^2 of 0.71 in this study is consistent with many nitrogen trace gas experiments from various soil and crop types which have reported R^2 values ranging between 0.42 and 0.87 (Sullivan *et al.*, 1996; Thornton *et al.*, 1997; Roelle *et al.*, 1999; Roelle and Aneja, 2002).

The four data points (solid squares) surrounding the solid line in Fig. 5 represent the control plots (no slurry applied to the plot) from this (Spring 2001) measurement
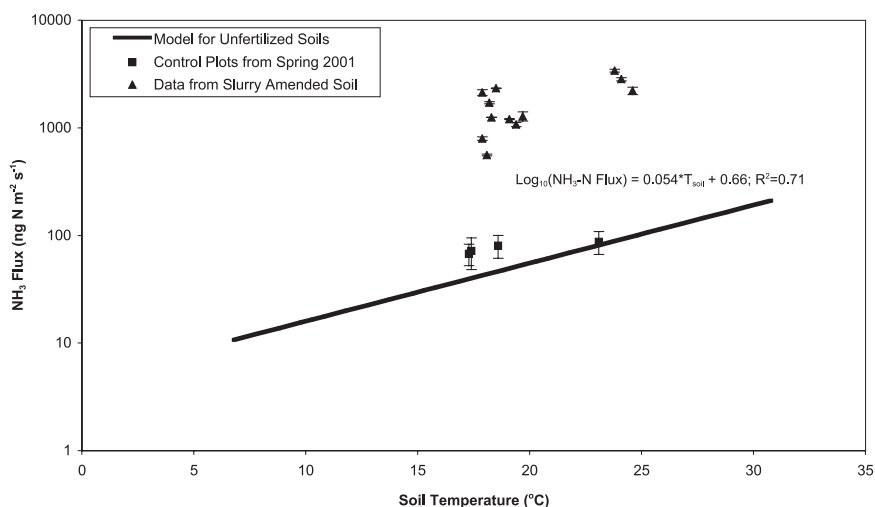

Figure 5. Measured NH_3-N flux vs. soil temperature. The solid line represents a temperature-based algorithm developed as part of an earlier study (Roelle and Aneja, 2002). The solid squares represent the control plots from spring 2001 measurements while the solid triangles represent the NH_3-N flux from the slurry applied soils. Vertical bars represent one standard deviation of the NH_3 flux.

campaign. These data points fit the general form of the model, and in fact, including these four new data points into the model, changes the R^2 only slightly from 0.71 to 0.70. The 12 data points (solid triangles) in this graph represent the data from the Spring 2001 slurry amended plots. Although these 12 data points did fall within the range of soil temperatures used to develop the empirical model, attempting to estimate the fluxes from the slurry amended plots using the empirical model in Fig. 5 would result in an underestimation of at least an order of magnitude. An empirical model developed from only the slurry amended soil data results in an $R^2 = 0.26$ and a new empirical relationship taking all data points (amended and nonamended) into account results in a decreased R^2 value from 0.71 to 0.39.

These results highlight that temperature will explain over 70% of the variability in NH_3 emissions when it is developed from, and applied to, soils that have not been recently amended (fertilized). However, similar empirical models relating temperature to NH_3 flux developed from recently amended soils or a combination of both amended and nonamended soils reduces the explanatory capability of the model to 26 and 39%, respectively. This suggests that when nitrification/denitrification, plant uptake, and immobilization are sufficiently small to be neglected in comparison to the chemical and physical processes during time periods immediately following slurry application, than temperature alone can not adequately estimate the NH_3 flux. During nonfertilized episodes, this relationship can be attributed to the fact that the bio-

chemical reaction rates of micro-organisms responsible for the production/consumption of NH_3 respond to changes in temperature (Sullivan *et al.*, 1996; Roelle *et al.*, 1999, 2001; Warneck, 2000). However, during recently fertilized events, as shown through the development of the mass transfer model, parameters other than temperature such as ammoniacal nitrogen content and pH must be considered.

Similar to the empirical model, the mass transport model relates the NH_3 flux to soil temperature (exponential dependence). Maintaining all other parameters constant (typically observed agronomic values before$_{(1)}$ and after$_{(2)}$ slurry application: $NH_{x(1)} = 6$ $\mu g/g$; $pH_{(1)} = 5.5$; $K_{(1)} = 3.69 \times 10^{-3}$ m s^{-1}; $NH_{x(2)} = 90$ $\mu g/g$; $pH_{(2)} = 6.5$; $K_{(2)} = 3.69 \times 10^{-3}$ m s^{-1}) and varying the temperature between 16.3 and 20.6°C (typical range during a measurement period) in both the mechanistic and empirical model produces similar profiles, yet at different magnitudes (Fig. 6). The average NH_3 flux measured before and after slurry application was 54 and 1724 ng N m^{-2} s^{-1}, respectively. Although soil temperatures from the different seasons did overlap, it is apparent that a temperature-based empirical relationship will fail to capture the magnitude of the emissions. While Fig. 6 reemphasizes the exponential dependence of NH_3 flux on soil temperature, it also highlights the role that other parameters, namely pH and ammoniacal nitrogen, must play in the mass transfer equation.

Applying the mechanistic model to the nonamended field site data collected during the Spring and Winter
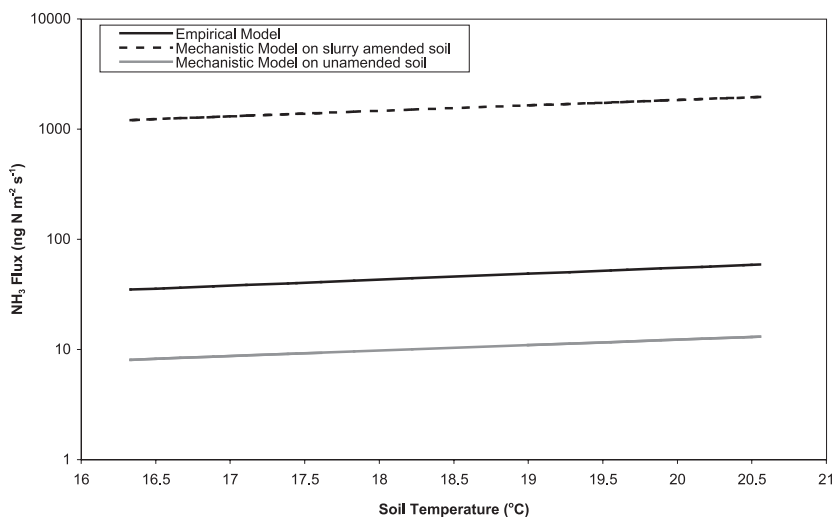

Figure 6. Modeled NH_3-N flux vs. soil temperature. The solid line represents the empirical model and the shaded (1) and dashed (2) lines represent a mechanistic model with all parameters constant at: $NH_x(1) = 6$ mg/g; $pH(1) = 5.5$; $K(1) = 3.69 \times 10^{-3}$ m s^{-1}; $NH_x(2) = 90$ mg/g; $pH(2) = 6.5$; $K(2) = 3.69 \times 10^{-3}$ m s^{-1}. Soil temperature was varied between 16.3 and 20.6°C.

2000 measurement campaign (Fig. 7, first 10 data points) results in much weaker model performance than when the mechanistic model is used for time periods immediately following slurry application (Fig. 7, last 4 data points). The average percent difference between modeled and measured values for the slurry amended plots was 16%, while the average percent difference for non-amended plots was 164%. This weaker relationship for the nonamended plots is explained by the fact that the assumptions in deriving the mechanistic model were than nitrification/denitrification, plant uptake, and immobilization processes were much slower than the volatilization processes, and that ambient $[NH_3]$ were negligible, all of which are invalid assumptions during the unamended measurement period. Therefore, during the slurry-amended measurement periods, it is important to consider the other controlling parameters from the mass transfer equation.

Based on measured wind speeds and temperature during this measurement period, the mass transfer coefficient ranged from 1.5×10^{-3} m s^{-1} to 2.4×10^{-3} m s^{-1}, as opposed to the experimentally measured value of 3.69×10^{-3} m s^{-1}. Results using the same soil conditions and the calculated mass transfer coefficient from Equation (21) are also plotted in Fig. 7. From the results of this study, the experimentally measured mass transfer coefficient is more accurate in estimates of the NH$_3$ flux. This may confirm that in soil environments, NH$_3$ emissions are limited more by rate of

diffusion of the NH$_3$ to the soil/air interface than by wind speed or temperature, as suggested by Sherlock and Goh (1985).

Ammoniacal nitrogen content and pH

Figure 8 shows both the daily trend of the NH$_3$-N content of the soil (primary axis) and the averaged NH$_3$ flux from the three sample plots on each of the successive measurement days (secondary axis). The solid squares in Fig. 8 represent the average flux from the control (unamended) plots). The decreasing trends in both NH$_3$-H flux and NH$_x$ content of the soil are expected based on the fact that as volatilization of NH$_3$ from the soil continues, in the absence of other NH$_3$ production mechanisms, there will be progressively smaller concentrations of NH$_3$ in the soil. To examine how changes in $[NH_x]$ effect the NH$_3$ flux predicted by the mechanistic model, all parameters in the mechanistic model are kept constant ($T = 20°C$; pH $= 6.5$; $K = 3.69 \times 10^{-3}$ m s^{-1}) and only the $[NH_x]$ is varied (Fig. 9). This modeled linear relationship is supported by an earlier study conducted by Roelle and Aneja (2002) during a nonfertilized period, which showed the NH$_3$ flux from the soil being highly correlated to the NH$_3$-N content of the soil [NH$_3$ Flux $= 55.5 \cdot (NH_x) - 160$; $R^2 = 0.86$]. Using this empirical relationship, which is based on soil conditions with much smaller [NH$_x$ $-$ N] (<9 μg/g compared to $\sim$105 μg/g) results in significantly higher NH$_3$ flux estimates (solid
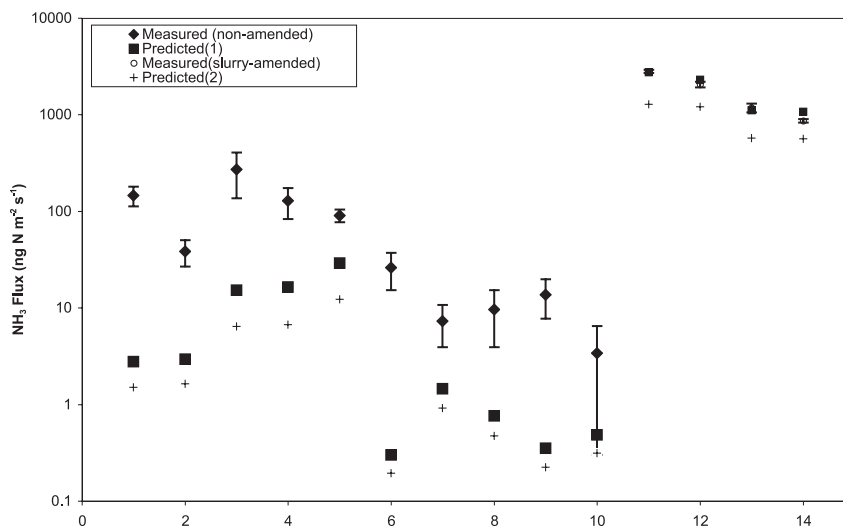

Figure 7. Plots of measured and predicted (mechanistic model) NH$_3$-N flux on different measurement days. The first 10 data points represent the nonamended plots, while the last four data points represent the slurry amended plots. Predicted (1) are estimated using $K = 3.69 \times 10^{-3}$ m s^{-1} while Predicted (2) calculates K from Equation (21).
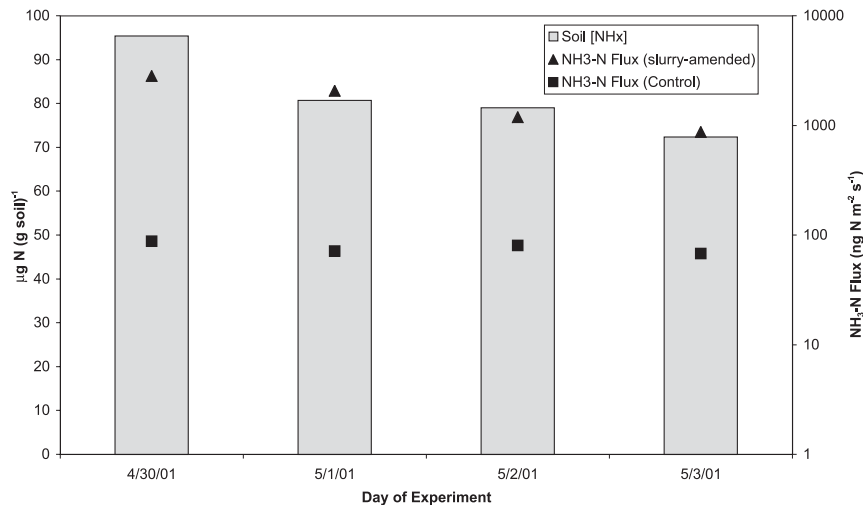
Figure 8. NH_x-N content (primary axis) and NH_3-N Flux (secondary axis) vs. the day of the experiment. Solid triangles represent the daily averaged NH_3-N flux from the slurry amended plots, while the solid squares represent the daily averaged NH_3 flux from the control (unfertilized) plots.

line) than the mechanistic model for values of $[NH_x]$ greater than approximately 5 $\mu g/g$.

Producing a new empirical model $[NH_3 \text{ Flux} = 22.7 \cdot (NH_x) - 91.4; \quad R^2 = 0.75]$ taking both the slurry-amended and nonslurry-amended soils into account shows that the soils ammoniacal nitrogen content is significant ($p < 0.01$) in estimating NH_3 emissions both prior to and after slurry application. The shaded and dashed lines in Fig. 9 differ by approximately 40% at lower values of NH_x (~ 10 $\mu g/g$) and less than 7% at the higher values of NH_x (~ 120 $\mu g/g$). Although it appears that the mechanistic and empirical models yield approximately equivalent flux estimates, it should be noted that in this example the pH was kept constant in the mechanistic model. While many field studies have found pH to remain fairly uniform throughout nonfertilized periods,
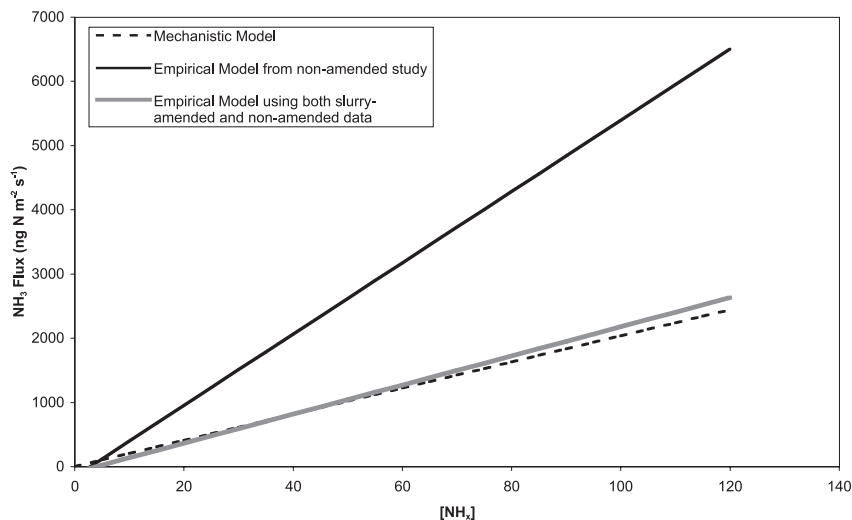

Figure 9. NH_3 flux vs. ammoniacal nitrogen content of the soil. The solid line represents the mechanistic model, and the dashed and shaded lines represent empirical models from the nonamended and combined data sets, respectively. All values kept constant at $T = 20°C$; pH = 6.5; $K = 3.69 \times 10^{-3}$ m s^{-1}.

this assumption is invalid during periods immediately following fertilization (Sullivan *et al.*, 1996; Li *et al.*, 1999; Roelle *et al.*, 1999).

As slurry is initially applied to the soil it is rapidly hydrolyzed to produce ammonium and carbonate ions, which causes an increase in the soil pH. As the ammonia volatilizes, H^+ ions accumulate in the soil and throughout the volatilization event there is a gradual decrease of the soil pH. Therefore, during recently fertilized episodes, pH and $[NH_x]$ cannot be considered in isolation because a change in $[NH_x]$ causes a change in the pH. This effect can be seen clearly in Table 2, which shows the pH beginning at approximately 6.6 for the amended plots and gradually decreasing to 6.2, while the control plot is assumed, based on previous studies, to remain fairly constant at 5.4.

While the overall change during these 4 days is less than $^1/_2$ of a pH unit, the effects on the estimated ammonia flux can be large. Based on the mass transport model, changing only the soil pH by 1 unit and maintaining all other variables constant at ($T = 20°C$, $NH_x = 90$ $\mu g/g$, $K = 3.69 \times 10^{-3}$ m s^{-1}) results in changes of NH_3 flux of approximately an order of magnitude (Fig. 10, solid line). However, in a more realistic situation, varying both the pH and $[NH_x]$ (as shown on the secondary axis) results in the NH_3 flux as seen in Fig. 10 (solid squares).

Figure 11 shows the measured NH_3-N volatilized as a % of the N applied. At a rate of N-application of 33 Kg N ha^{-1}, nearly 20% of the applied N is lost as NH_3 within the first 4 days after application. The predicted NH_3-N volatilized as a % of the N applied is shown by the solid line in Fig. 11, which is based on the daily averaged soil parameters measured and the mass transfer equation with the constant mass transfer coefficient (3.69×10^{-3} m s^{-1}). The solid line appears to accurately predict the percent of N lost as NH_3 during the first 3 days following slurry application. However, while the measured rate of loss begins to level out at approximately 20%, the solid line (predicted value) tends to be increasing, although at a slower rate. Other modeling and experimental studies have found that the percent of N applied, which is lost as NH_3 typically levels out at approximately 30%, and that this usually occurs within the first 1–2 weeks after fertilizer application (Singh and Nye, 1986b, 1988). While the NH_3 volatilized (as a percent of the N applied) in this study appears to level out slightly faster than other reported studies, this may be a factor of the amount of nitrogen initially applied to the soil. Whereas, the Singh and Nye (1986a) study applied nearly 210 kg N ha^{-1}, this study applied 33 kg N ha^{-1}. Furthermore, the $[NH_x]$ was still elevated (in comparison to background levels) at the conclusion of the measurement period, indicating that this volatilization event may have persisted for a few more days. Regardless, the consistent trend among the model, measurements, and previous lab and field studies indicates that these volatilization events are short-lived (few days to 2 weeks), and generally result in emissions of 20–30% of the applied nitrogen.
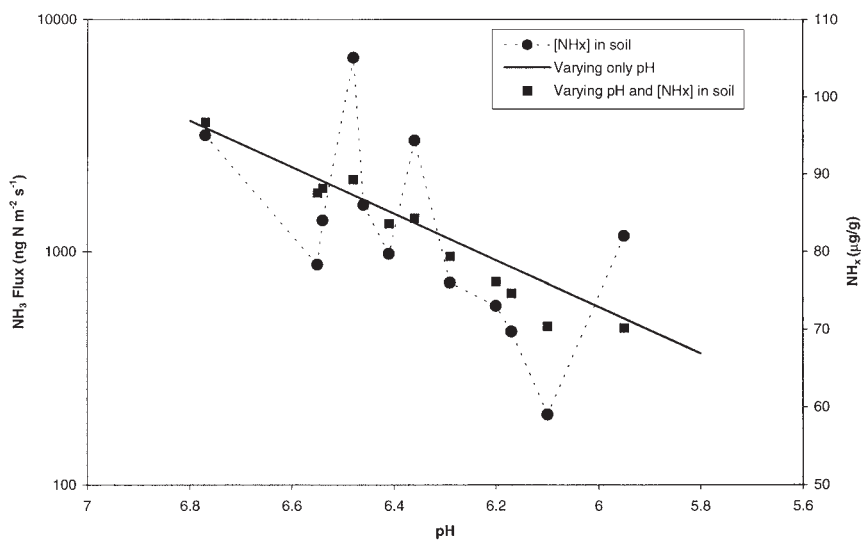

Figure 10. NH_3 flux vs. soil pH. Solid line represents the mechanistic model, and only varying the pH. All values in the model are kept constant at $T = 20°C$; $NH_x = 90$ mg/g; $K = 3.69 \times 10^{-3}$ m s^{-1}.

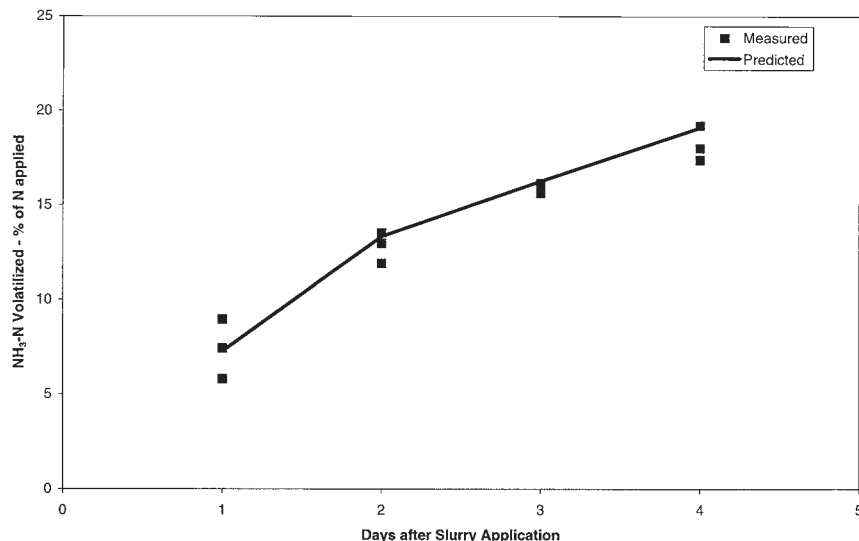**Figure 11.** NH$_3$-N volatilized as a percent of the N applied. Solid squares represent the measured values from each plot on the four measurement days. The solid line represents the modeled NH$_3$-N volatilized using the soil parameters measured.

CONCLUSIONS AND RECOMMENDATIONS

Using a mechanistic/mass transport model and measured soil parameters, ammonia emissions were estimated and compared to calculated flux values at an eastern North Carolina swine farm. A mechanistic model developed for volatilization events performed well (average of 16% difference between modeled and measured flux values) immediately following a slurry application, however, performed poorly on the nonamended soils (average of 164% difference between modeled and measured flux values). This relationship is not surprising, given that the assumptions in the mass transport model, namely negligible plant uptake and ammonification processes relative to the ammonia in the soil/slurry mixture, both of which (plant uptake and ammonification processes) are not valid assumptions during periods prior to or long after slurry/fertilizer application. Further, during time periods prior to slurry application the assumption of ammonia concentration in the air being negligible in comparison to the ammonia concentration in the soil cannot be assumed to be valid, and therefore ammonia concentrations in the air must be included in the mass transfer model.

In this study, the value of the mass transfer coefficient was kept constant at 3.7×10^{-3} m s^{-1} based on laboratory results reported by Singh and Nye (1986b) and research conducted by other investigators. Using an equation to describe the exchange coefficient in terms of wind speed and temperature resulted in calculated exchange coeffi-

cients ranging from 1.5×10^{-3} m s^{-1} to 2.4×10^{-3} m s^{-1}. The literature currently describes mass transfer coefficients ranging from 1.3×10^{-6} m s^{-1} to 1.2×10^{-2} m s^{-1}, and therefore, a more thorough understanding of this parameter must be obtained. The fact that the experimentally measured exchange coefficient performed better than the calculated exchange coefficient may indicate that for soil systems the NH$_3$ flux is rate limited by diffusion to the soil/air interface as opposed to wind speed or temperature. Soil ammoniacal nitrogen content was found to be linearly related to NH$_3$, while pH and temperature were both found to have an exponential dependence. The measurements revealed that the applied N is lost at the greatest rate in the first 2 days following application, and begin to level out by day 4, although additional field data is required to confirm this relationship.

While the currently used emission factor approach may adequately capture the total NH$_3$ emitted to the atmosphere on a yearly basis, these results show that they would perform poorly in resolving any temporal or spatial trends. In an effort to further refine global Nitric Oxide (NO) emission estimates, Yienger and Levy (1995), Fierer and Schimel (2002), and Ridolfi *et al*. (2003) have proposed a "pulsing" mechanism to account for the large bursts of NO following the wetting of dry soils. Similarly, it would appear that a mechanism should be incorporated into the emission estimate process to further refine the budget of ammonia emissions from soils, especially intensively managed soils which are consistently amended with both commercially derived fertiliz-

ers and animal waste. As a first approach during non-amended periods, the temperature-based model appears to capture the majority of the variation in NH_3 emissions. A possible approach for the amended periods would be to adopt the same procedures commonly used in the estimates of biogenic NO emissions, which is to apply a temperature algorithm and a factor to adjust for the amount of fertilizer the crop receives. Unfortunately, this approach requires a large set of data conducted over many different soil and crop types to empirically determine these factors, which, to date, is still unavailable.

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